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On: 20 August 2012, At: 22:08

Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

Degradation of Organic Photochromes: Light-Promoted and Dark Reactions

V. Malatesta^a

^a Great Lakes Chemical Italia, Via Maritano 26, 20097 S. Donato, Milano, Italy

Version of record first published: 24 Sep 2006

To cite this article: V. Malatesta (1997): Degradation of Organic Photochromes: Light-Promoted and Dark Reactions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 69-74

To link to this article: <http://dx.doi.org/10.1080/10587259708036144>

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DEGRADATION OF ORGANIC PHOTOCHROMES: LIGHT-PROMOTED AND DARK REACTIONS

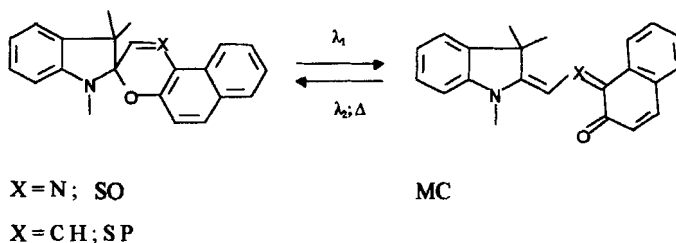
V. MALATESTA

Great Lakes Chemical Italia, Via Maritano 26, 20097 S. Donato (Milano), Italy

Abstract: Degradation processes limit the number of darkening \rightleftharpoons bleaching cycles that functional photochromic dyes spirooxazines (SO) and spiropyrans (SP) can sustain. Beside photochemical photooxidation, degradative processes based on dark reactions that include electron-transfer to organic and inorganic acceptor, trapping of free radical species, and reactions with nucleophiles substantially limit the useful lifetime of these dyes. The ability of spiro- and/or merocyanine forms to sensitize formation of singlet oxygen ($^1\text{O}_2$) is rather poor and the chemical reactivity of both their closed and open form toward $^1\text{O}_2$ sluggish.

INTRODUCTION

Spiropyrans (SP) and spirooxazines (SP) are among the most well known organic photochromes¹. Many useful applications have been envisaged in several important areas, including high-density optical storage, optical switching, image processing and displays. Exposure of SO's and SP's in solution or in a polymer matrix to UV-A or sunlight results in a color change due to the formation of a deeply colored merocyanine (MC) form that tends to revert back to the closed spiro form either thermally² or photochemically³.

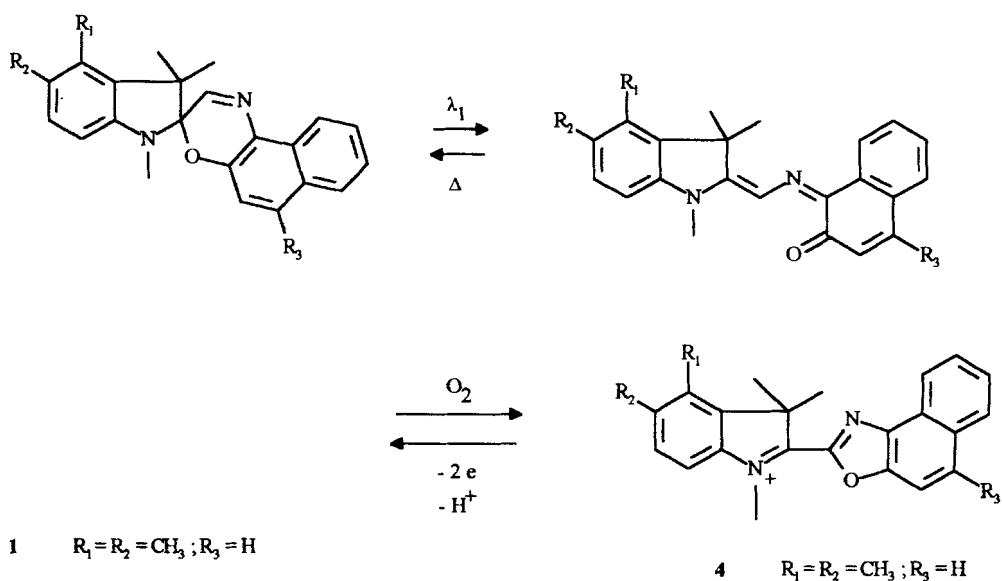


SCHEME 1

Full reversibility of the photochromic phenomenon is however only an ideal situation as photochemical oxidation, degradative processes based on dark reactions that include, electron- transfer to organic and inorganic acceptors, trapping of free radical species and reactions with nucleophiles substantially limit the useful lifetime of these dyes. We shall briefly discuss these four topics with the intent of showing the inherent difficulties that have to be faced when trying to design new stable photochromic molecules.

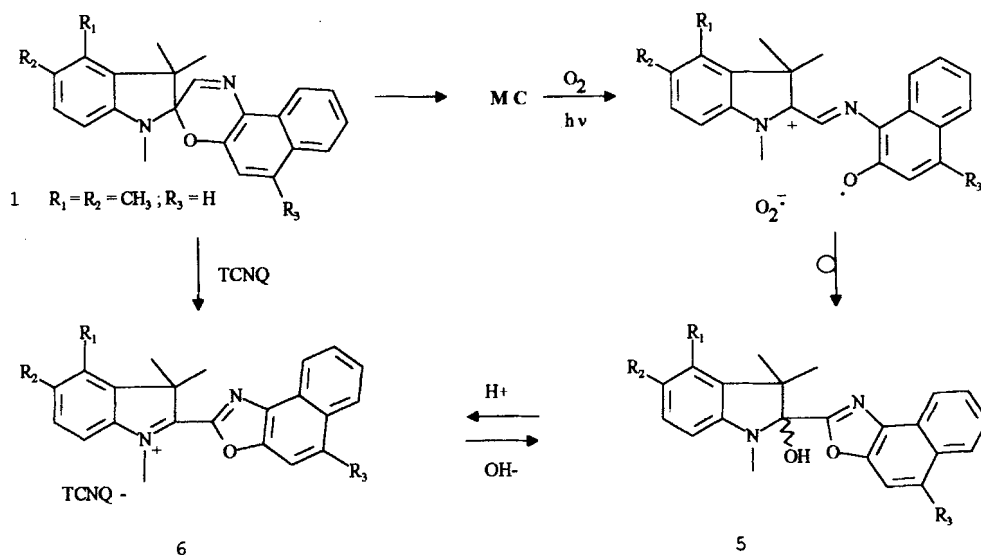
DISCUSSION

Photooxidation and Dark Oxidation Reactions. Prolonged exposure of a typical spirooxazine (SO) **1** (Scheme 2) air-equilibrated acetonitrile (ACN) solution to UV light results in a irreversible change⁴ of the deep blue merocyanine (MC) to yield a greenish and then yellow fluorescent color due to compound **4**.



SCHEME 2

The same color change is observed when operating in de-aerated ACN solutions in the presence of suitable electron acceptors such as e.g. 7,7,8,8-tetracyanoquinodimethane (TCNQ)⁵. The thermal reaction between **1** and TCNQ (10^{-3} M; 1:2 ratio) in Ar-purged refluxing acetonitrile provides a complex salt that crystallizes as dark green platelets exhibiting semiconducting behavior (Scheme 3):

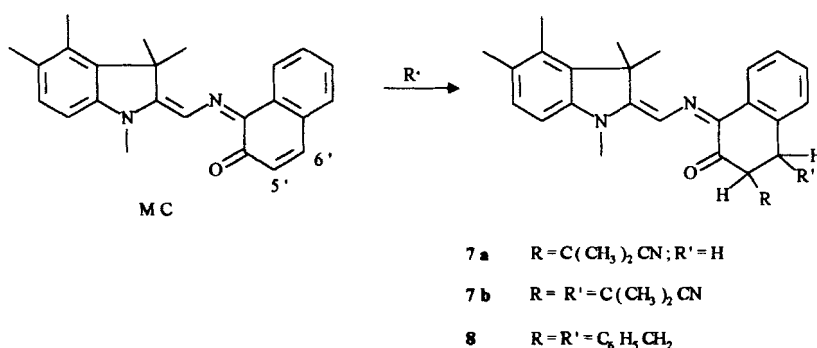


SCHEME 3

Compound **6** may form in a reversible fashion from **5** by acidic treatment. This novel finding evidences that the photooxidative route and the thermal hypoxic oxidation lead to the same degradation product, namely **6**. Spirooxazines **2** and **3** behave similarly to yield the correspondent complex salt whose structure has been assigned by NMR spectroscopy⁵.

Reductive Degradation Reactions. The metastable merocyanine form MC reacts easily with free radicals derived from adventitious radical sources or residual polymerization initiators. Indeed when photochromic polymethylmetacrylate sheets are prepared thermally or photochemically from a methylmethacrylate (MMA) solution of **1** in the presence of free-radical initiator 2,2'-azobis(isobutyronitrile) (AIBN) a reddish-violet poly-

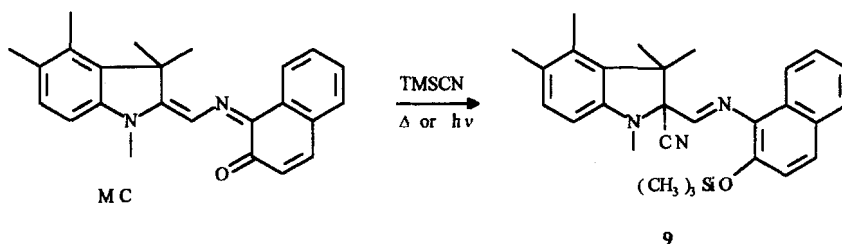
methylmethacrylate (PMMA) matrix is isolated. The same coloration is observed⁶ by heating a ACN solution of **1** containing a few ppm of AIBN. Free radical mono- and di-adducts **7a** and **7b** are formed that have strong absorptions at 520 nm ($\log \epsilon = 4.68$) and 542 nm ($\log \epsilon = 4.15$) respectively (Scheme 4):



SCHEME 4

Benzyl radicals formed by hydrogen abstraction from toluene with tert-butoxy radical have also been trapped with **1** and the di-adduct **8** isolated. Its absorption maximum is at 518 nm ($\log \epsilon = 4.17$). The easy reactivity of spirooxazines with free radicals seriously affects their durability especially when they are used in organic polymeric matrices prepared by casting.

Reaction with Nucleophiles. A fast, clean reaction occurs when ACN solutions of **1** and tri-methylsilylcyanide (TMSCN) are heated at 40°C or photolyzed with a UV lamp at ambient temperature⁷. The TMSCN adduct **9** forms in quantitative yields and results from an unprecedented 1,6 Michael-type addition of TMSCN onto the doubly conjugated carbonyl of the MC of **1** (Scheme 5):



SCHEME 5

The same reaction has been observed for spiropyrans⁷.

Reaction with Singlet Oxygen. It has been shown⁴ that SO's and SP's are in general unable to sensitize, in their closed spiro or open merocyanine form, formation of singlet oxygen $^1\text{O}_2$. Furthermore even when singlet oxygen is produced by using typical sensitizers such as Rose Bengal or Methylene Blue, its reactivity on both the closed or open form is responsible only marginally for their photooxidation^{4,8}.

CONCLUSIONS

The above reported easy reactivity of the MC form of SO's and SP's indicates how difficult a task is for the organic chemist to design structures whose MC form is endowed with a inherent stability. To achieve this, oxygen, free radicals and nucleophilic agents should be carefully and thoroughly removed from SP and SO photochromic systems. It is however anticipated that some other kind of so far unreported reactions will negatively affect the durability of these classes of photochromes. Apparently their chemical weakness stems from the richness of the fully conjugated π electronic structure of the merocyanine forms that makes them prone to easily undergo electron transfers and to the attack of nucleophilic agents being they radicals or ions.

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